MONOLAYERS OF 11-TRICHLOROSILYLUNDECYL THIOACETATE: A SYSTEM THAT PROMOTES ADHESION BETWEEN SILICON DIOXIDE AND EVAPORATED GOLD

S. R. Wasserman, H. Biebuyck, and G. M. Whitesides*
Department of Chemistry
Harvard University
Cambridge MA   02138

AD-A208 266

Technical Report No. 16 (May 1989)

Interim Technical Report

(Accepted for publication in <u>J. Mat. Research</u>)

DTIC
ELECTE
S
MAY 3 1 1989
D

The views and conclusions in this document are those of the authors and should not be interpreted as necessarily representing the official policies, either expressed or implied, of the Defense Advanced Research Projects Agency or the U.S. Government.

89 5 30 165

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION	1b. RESTRICTIVE MARKINGS
Unclassified	

2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION / AVAILABILITY OF REPORT
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE	Approved for public release; distribution unlimited

4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S)
Technical Report # 16	

6a. NAME OF PERFORMING ORGANIZATION	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION
Harvard University		Office of Naval Research

6c. ADDRESS (City, State, and ZIP Code)	7b. ADDRESS (City, State, and ZIP Code)
Office of Sponsored Research Holyoke Center, Fourth Floor Cambridge MA 02138-4993	Code 1130P 800 North Quincy Street Arlington VA 22217-5000

8a. NAME OF FUNDING / SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
ONR/DARPA		

8c. ADDRESS (City, State, and ZIP Code)	10. SOURCE OF FUNDING NUMBERS			
	PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO
800 North Quincy Street Arlington VA 22217-5000	85-K-0898	NR 356-856		

11. TITLE (Include Security Classification)
"Monolayers of 11-Trichlorosilylundecyl Thioacetate: A System that Promotes Adhesion between Silicon Dioxide and Evaporated Gold"

12. PERSONAL AUTHOR(S)
Wasserman, S. R.; Biebuyck, H.; Whitesides, G. M.

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Interim	FROM _____ TO _____	May 1989	

16. SUPPLEMENTARY NOTATION

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	adhesion, silicon, gold, monolayer, self-assembly

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

The use of sulfur-containing organic monolayer films improves adhesion between gold and silicon dioxide. The structures of these monolayers were analyzed using contact angle, ellipsometry, and XPS. The zone of adhesive failure was at or near the gold-monolayer interface.

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
[X] UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	

22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL
Dr. Joanne Milliken		

DD FORM 1473, 84 MAR   83 APR edition may be used until exhausted.   SECURITY CLASSIFICATION OF THIS PAGE
All other editions are obsolete

Monolayers of 11-Trichlorosilylundecyl Thioacetate: A System that Promotes Adhesion Between Silicon Dioxide and Evaporated Gold

Stephen R. Wasserman, Hans Biebuyck, and George M. Whitesides*

Department of Chemistry, Harvard University, Cambridge, MA 02138

- 1 -

Abstract

The use of sulfur-containing organic monolayer films improves adhesion between gold and silicon dioxide. The structures of these monolayers were analyzed using contact angle, ellipsometry, and XPS. The zone of adhesive failure was at or near the gold-monolayer interface.

Introduction

This chapter describes the use of sulfur-containing organic monolayers to improve the adhesion of gold to silicon substrates having a native silicon dioxide surface layer. Gold adheres to clean silicon,[1] but not to silicon dioxide.[2] The affinity of gold toward silicon dioxide can be improved by coating with chromium[3] or titanium[3] films or by adding interlayers containing fluoride salts.[4] Bombardment of gold-covered silicon dioxide with electrons[5] or heavy ions[6,7] also enhances adhesion. Thin (< 100 Å) covalently-bonded alkylsiloxane films containing amines or epoxides improve the adherence of gold to glass.[8]

Gold surfaces have a high affinity for alkyl thiols (RSH),[9,10] dialkyl sulfides (R$_2$S),[11,12] and dialkyl disulfides (RSSR).[13] The mechanisms of bonding between organic sulfur compounds and gold have not been clearly established although surface gold thiolates have been suggested as important.[13,14] Allara and Nuzzo have exploited the affinity of gold for sulfur by using a relatively thick organic polysiloxane layer containing a disulfide to improve the adhesion of gold to alumina and silicon dioxide.[15,16]

We have shown previously that monolayers can be used to promote adhesion.[17] Here we demonstrate that covering a Si/SiO$_2$ substrate with a covalently attached organic monolayer film containing thiol groups (and possibly disulfides derived from them) or thioacetate groups improves the adhesion of gold to the substrate.
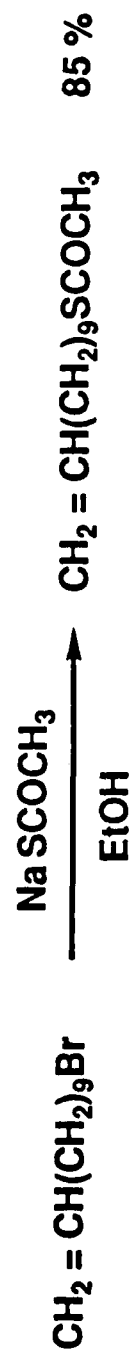
Results

Preparation of Monolayers. The molecular precursor to the desired monolayer was 11-trichlorosilylundecyl thioacetate, $Cl_3Si(CH_2)_{11}SCOCH_3$, **1**. Scheme I outlines the synthesis of **1**. We protected the thiol group as a thioacetate to prevent reaction of free thiols with chlorosilane groups. Substrates for these experiments consisted of standard boron-doped semiconductor grade silicon wafers. These wafers were cleaned by heating in a mixture of 30% H_2O_2 and conc. H_2SO_4,[18] and stored under water until use.

Figure 1 summarizes the preparation of the composite thin films. The thioacetate monolayers were assembled by immersing the wafers in freshly prepared solutions of **1** in methylene chloride.[19] We prepared control samples consisting of alkylsilane groups having no sulfur-containing functionality from hexadecyltrichlorosilane (HTS, $Cl_3Si(CH_2)_{15}CH_3$).[20] The thioacetate groups (-SCOCH_3) in monolayers derived from **1** were hydrolyzed to thiols (-SH) using hot conc. aqueous HCl (Figure 1).[21]
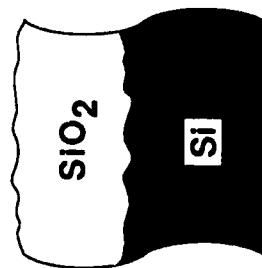
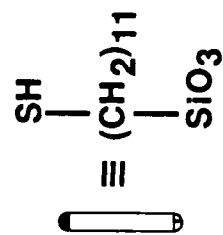**Characterization of Monolayers: Contact Angle, Ellipsometry, and X-Ray Photoelectron Spectroscopy (XPS).** The advancing contact angle of water on monolayers derived from **1** was θ_a^{H2O} = 78-80°; that for hexadecane (HD) was θ_a^{HD} = 0°. Hydrolysis of the ester and release of the thiol changed θ_a^{H2O} only slightly to 72-74°. For comparison, θ_a^{H2O} is ~ 70° for self-assembled monolayers

Scheme I. Synthesis of 11-trichlorosilylundecyl
thioacetate, **1**.

$$CH_2 = CH(CH_2)_9Br \xrightarrow[\text{EtOH}]{\text{Na SCOCH}_3} CH_2 = CH(CH_2)_9SCOCH_3 \quad 85\%$$

$$\xrightarrow[\text{cat. H}_2\text{PtCl}_6]{\text{HSiCl}_3} Cl_3SiCH_2(CH_2)_{10}SCOCH_3 \quad 56\%$$
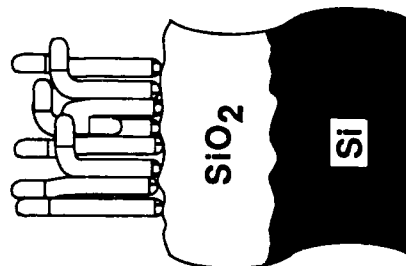
Figure 1. Schematic representation of the preparation of the gold-silicon composite. (A) Formation of a thioacetate-terminated monolayer on Si/SiO_2 by reaction of $Cl_3Si(CH_2)_{11}SCOCH_3$ (**1**) in methylene chloride solution with Si-OH groups and adsorbed water on the surface of the substrate. (B) Formation of a thiol-terminated monolayer by acidic hydrolysis of the monolayer prepared in step A. (C) Thermal evaporation of gold (650-1000 Å) onto the thiol-terminated monolayer prepared in step B. The molecular order in these monolayer systems has not been defined, but the monolayers were thinner (and thus probably more disordered) than fully _trans_-extended chains oriented perpendicular to the surface.

of HS(CH$_2$)$_{12}$SCOCH$_3$ on gold.[10] No monolayer system has been
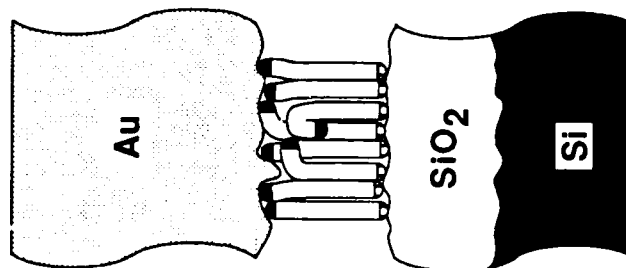prepared that presents a densely packed array of -SH groups.
Experimental values for contact angles on such systems are
thus not available.

Ellipsometric measurements indicated that the monolayers
derived from **1** were 11-15 Å thick.[22] This value is less than
the 20 Å that we would expect for a fully _trans_-extended
alkyl chain oriented perpendicular to the Si/SiO$_2$ surface.[23]
The structure of these monolayers probably corresponds to a
fairly disordered liquid-like layer, rather than one that
contains quasi-crystalline islands.[24] While the monolayers
prepared from **1** were not close-packed structures, we
demonstrate below that the effective density of
thiol/disulfide groups was sufficient to achieve our goal of
promoting adhesion to gold. On hydrolytic removal of the
acetate group, we observed a 0-2 Å decrease in the thickness
of the monolayer (~ 2 Å would have been expected).[25] This
change, while consistent with that expected for removal of an
acetate group, is small and is within the limits of
uncertainty of the ellipsometric method.

The XPS spectra for these monolayers (Figure 2)
demonstrate that the elemental compositions of the monolayers
were those expected. Survey spectra indicated the presence
of only oxygen, silicon, carbon, and sulfur on the surface.
Both the monolayer from **1** and that obtained from it by
hydrolysis contained no chlorine: hydrolysis of the Si-Cl

Figure 2. XPS spectra of monolayers prepared from

$Cl_3Si(CH_2)_{11}SCOCH_3$ (**1**) and $Cl_3Si(CH_2)_{15}CH_3$ (HTS)

on Si/SiO_2 substrates: survey spectra (left) and

high resolution spectra of the carbon 1s (left

center), sulfur 2s (right center), and gold 4f

(right) regions. Spectra are shown for these

monolayers prior to evaporation of gold onto the

sample (A,C,E) and for the monolayers that

remained after the gold had been removed from the

surface (B,D,F) (see text). Spectra are

referenced to an average of the binding energies

of the C 1s, Si 2p, and O 1s peaks. The C 1s and

S 2s spectra are each normalized to the same

maximum peak height. The Au 4f spectra are not

normalized; their intensities represent the

relative amounts of gold remaining on these

surfaces. The S 2s spectra have been smoothed

using a nine-point algorithm with a symmetrical

triangle convolution function. (A. Savitzky, M.

J. E. Golay, Anal. Chem. **36**, 1627 (1964).)

(A) Thioacetate-terminated monolayer prepared from

1. (B) A after removal of gold from the surface.

The survey and Au 4f spectra include bulk gold

(Au(0)) in the area surrounding the region of

adhesive failure. (C) Thiol-terminated monolayer

prepared by acidic hydrolysis (conc. HCl, 70 °C, 1.5 h) of A. (D) C after removal of gold from the surface. (E) Methyl-terminated monolayer prepared from HTS. (F) E after removal of gold from the surface.
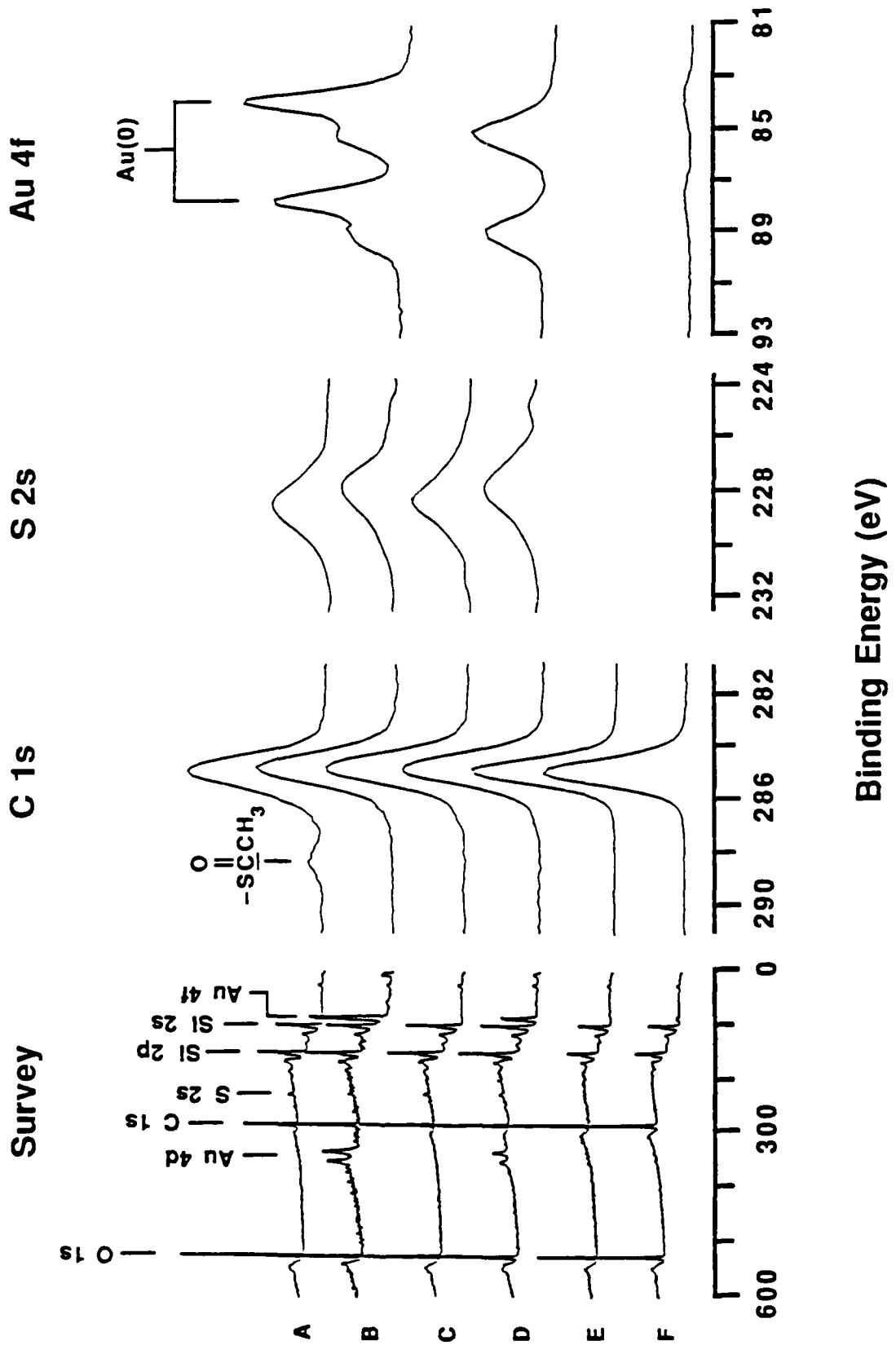
bonds was apparently complete. The monolayer from **1** showed a

C 1s peak at 288.2 eV, corresponding to the carbonyl carbon

of the -SCOCH3 group. After hydrolysis in conc. aqueous HCl,

the intensity of this peak had decreased to less than 20% of

its original value. The S 2s electrons present in the

monolayer before hydrolysis had a binding energy of 228.7 eV;

after hydrolysis this energy had not changed significantly

(< 0.3 eV).[26,27] The calculated atomic ratio of the C 1s

(-SC=O-) signal to that of sulfur in the unhydrolyzed

monolayer was approximately 1.2:1. Although this ratio

should be 1:1, these signals were weak and subject to

significant quantitative error.

The contact angle, ellipsometric, and XPS measurements

imply that adsorption of **1** onto silicon substrates containing

a surface oxide layer resulted in the formation of a loosely

packed monolayer containing a terminal thioacetate. Upon

acidic hydrolysis the protecting acetate group was removed,

resulting in a thiol- and/or disulfide-terminated interface.

The contact angle and ellipsometric measurements on the

thiol-terminated monolayer, as well as the continued presence

of sulfur in the XPS spectrum, established that the monolayer

was still bound to the surface after hydrolysis of the

protecting group.

**Preparation and Characterization of Gold-Coated
Substrates.** Gold layers (650-1000 Å) were formed by thermal

evaporation onto four types of samples: bare Si/SiO2

substrates and Si/SiO2 having attached monolayers from **1**

(containing -SCOCH$_3$ terminal groups), monolayers derived from **1** by hydrolysis (-SH and, perhaps, -SS- terminal groups), and monolayers from HTS (-CH$_3$ terminal groups). We evaluated the strength of adhesion of gold on these substrates semiquantitatively through peel tests using pressure sensitive tape (Table I). The tape was pressed into intimate contact with the gold overlayer and removed in a 180° test configuration at a rate of 1 mm/min. For both the bare Si/SiO$_2$ substrate and the substrate having a methyl-terminated monolayer, the strength of adhesion between the gold and the substrate was below our limits of detection. In the presence of both the -SH and -SAc-terminated monolayers, the adhesion strength was much greater. Adhesive failure on these samples occurred either at the interface between the tape and the gold or at the interface between the adhesive and the backing of the tape itself. No gold transferred to the tape; in some cases, visible residue from the adhesive in the tape remained on the gold surface. The adhesive strengths listed in Table 1 for these samples therefore are measurements of the strength of the gold-tape interface, rather than the apparently stronger gold-monolayer interface. At higher peel rates (100 mm/min) the sulfur-containing monolayers withstood forces of 400 g/cm.

While the interfaces between the gold and the sulfur-containing monolayers were strong enough to withstand these

Table I. Strength of Gold-Substrate Interaction as a
Function of the Chemical Composition of the
Substrate Surface.

Surface Composition[a]	Yield Strength (g/cm)[b]
(1) -SH	> 84
(2) $-SCOCH_3$	> 70
(3) $-CH_3$	< 1
(4) SiO_2	< 1

[a]For the first three entries the interface in contact with
the gold had the structure $Si/SiO_2/O_3Si(CH_2)_{11}R$, where
$R = -SH$, $-SCOCH_3$, and $-(CH_2)_4CH_3$. The last entry is for
Si/SiO_2 with no organic monolayer. The density of packing
and the degree of order within these structures was probably
$1 \approx 2 < 3$.

[b]For a peel test at 1 mm/min using pressure sensitive tape
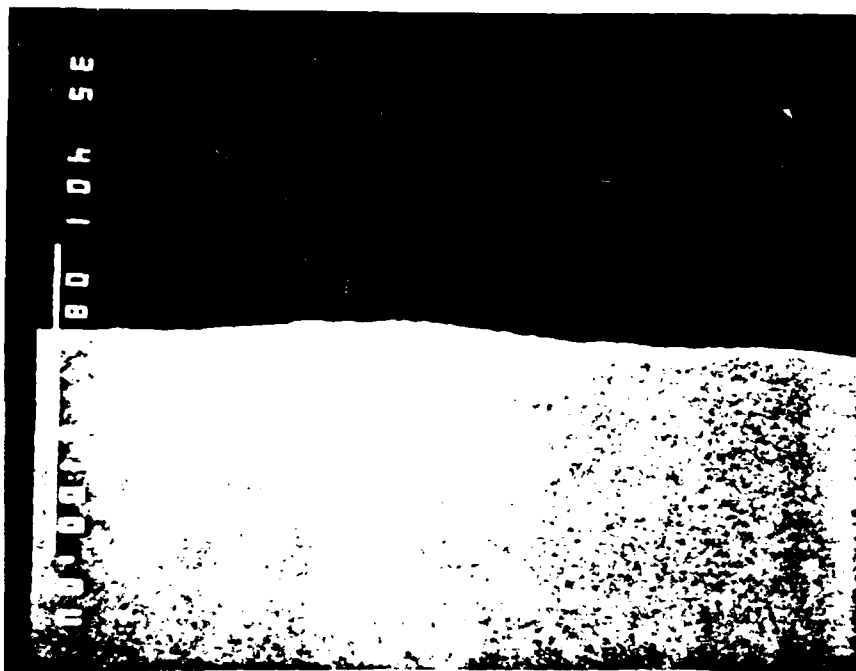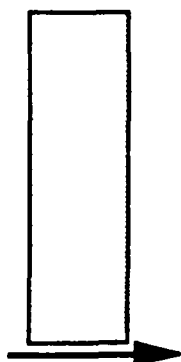and a 180° test configuration.

peel tests at low peel rates, we were occasionally able to cause failure in adhesion between the gold and the monolayer-coated substrate by pulling the tape rapidly by hand from the gold-covered surface. Failure under these conditions was not reproducible and we obtained surfaces after failure with drastically differing coverages of gold remaining on the substrate.[28]

Figure 3 presents scanning electron micrographs of the edge of the gold that remained on methyl- and thiol-terminated monolayers after adhesive failure. When peeling the tape from a methyl-terminated monolayer, all the gold in the region covered by the tape was removed. This process also detached gold from regions adjoining that covered by the tape. The extension of the region from which the gold had been removed beyond the edge of the tape indicated that the cohesion within the gold leaf exceeded the adhesion of the gold to the monolayer. The edges of the gold that remained on this surface were relatively straight and no macroscopic (> 10 μm) islands of gold were present in those areas previously covered by the metal overlayer.

When the tape was removed from a thiol-terminated monolayer, the total area of adhesive failure was significantly smaller than that observed for the methyl-terminated monolayer. In contrast to the latter surface, the zone of failure did not extend beyond the edge of the tape; that is, adhesion to the surface exceeded cohesion within the gold. The edges of the residual gold were irregular and

Figure 3. Electron micrographs of the border of the gold
remaining after adhesive failure. The light
regions are gold; the dark areas correspond to the
Si/SiO_2 substrate. The shaded region to the left
of each micrograph indicates that part of the
field of view which had been covered by the tape.
The size markers in the micrographs correspond to
100 μm. (A) Methyl-terminated monolayer prepared
from $Cl_3Si(CH_2)_{15}CH_3$ (HTS). The arrow indicates
the approximate position and direction of the edge
of the tape before its removal. The edge of the
gold corresponds to the edge of the tape.
(B) Thiol-terminated monolayer prepared by acidic
hydrolysis (conc. HCl, 70 °C, 1.5 h) of a
monolayer prepared from $Cl_3Si(CH_2)_{11}SCOCH_3$ (**1**).
The entire field of view was covered by the tape.
The edge of the gold represents the border of the
region where failure in adhesion had occurred, but
it does not correspond to the edge of the tape.

A

B

islands of gold remained in the regions that had been under the tape.

Figure 2 also shows XPS spectra of those regions of the substrate from which the gold film had been removed for methyl-, thioacetate-, and thiol-terminated monolayers. These spectra were acquired in regions which did not contain any gold islands that were visible by optical microscopy at 50x magnification. (The spectra for the thioacetate-terminated monolayer include bulk gold surrounding the region of failure.) Comparisons of these spectra with those obtained before the substrates were covered with gold showed, in general, no major changes in the ratios of carbon, oxygen, silicon, and sulfur. The acetate group had, however, disappeared from the thioacetate-terminated monolayer. Virtually no gold remained on the methyl-terminated surface: the intensity of the Au 4f peak corresponded to trace quantities and the atomic ratio of gold to carbon was Au/C = 0.003. Similar quantities of residual gold were inferred for the bare Si/SiO_2 substrate. Almost ten times as much gold was retained on the surface of the sulfur-containing monolayers: Au/C= 0.03 and Au/S = 0.9 - 1.0.[29] These observations confirm the results of the peel tests: the presence of sulfur in the monolayer significantly increases the affinity of the surface for gold. We note that, after stripping the gold layer from the sulfur-containing monolayers, approximately one atom of gold was retained for each sulfur atom on the surface.

On the sulfur-containing interfaces, we observed a single species of gold whose binding energy was 0.80 ± 0.1 eV higher than that of Au(0) and that of the gold which remained on both the bare Si/SiO$_2$ substrates and the methyl-terminated monolayers.[30] The sulfur remaining on the thiol- and thioacetate-terminated interfaces after the gold had been removed had a binding energy 0.65 ± 0.1 eV lower than that of the sulfur in the original thioacetate.[31] These observations suggest that the residual gold on the thiol-terminated surface was in an oxidized form relative to Au(0) while the sulfur was somewhat reduced relative to that in the starting monolayer.[32] The observed shift in the binding energy could also be explained by changes in the size of gold clusters that remain on the monolayer. On poorly conducting substrates the Au $4f_{7/2}$ binding energy for coverages less than 2 monolayers shifts to higher binding energy.[33] This shift, whose magnitude increases (up to 0.6 eV) as the gold coverage decreases, has been attributed to the positive charge that remains after photoemission. We do not for two reasons believe that this effect is relevant to this study. First, our substrates were of low resistivity (0.5-40 Ω) and we did not observe any effects of differential charging. Second, the gold remaining on the thiol interface had a higher binding energy than that of the even lower amounts of gold left on the methyl surface.

Discussion

Modification of the surface of a Si/SiO2 substrate by
covering it with a covalently bonded organic monolayer
containing thiol groups significantly enhances the adhesion
of evaporated gold to these substrates. Although this work
clearly establishes that incorporation of covalently attached
organosulfur compounds is a successful strategy for improving
adhesion, our samples showed some variability from region to
region. While we have not fully optimized the procedure nor
identified the reasons underlying the variability in results,
we offer two possible explanations for this irregularity.
First, contamination of the sulfur-containing interface
(probably by volatile organic compounds) may prevent
interaction between the gold and the sulfur. Second, the
strength of interaction between the sulfur and the evaporated
gold may depend on the rate at which the gold is deposited.
This rate could affect the degree of contact between the gold
and the monolayer, the temperature of the interface, or a
number of other factors influencing adhesion. We have used
evaporation rates of 2.5 and 10 Å/sec. Changing this rate
may result in more substantial adhesive interactions.

Since, during adhesive failure, the bulk of the gold was
removed while the monolayer was left apparently intact,
failure occurred at or near the monolayer-gold interface.
For the methyl-terminated monolayer, the failure within the
composite was probably sharply localized at the hydrocarbon-
gold interface. When the monolayer contained sulfur,

however, gold remained on the surface in quantities
approximately equal to sulfur (Au/S = 0.9-1.0) This
observation suggests that the zone of failure was located
within the gold itself, possibly between the first and second
monolayers of gold at the monolayer-gold interface. Such a
failure mode is possible if the gold-sulfur interface
actually consisted of a monolayer of Au(I) coordinated to the
sulfur. The formation of this type of interface is
represented by equation 1. This supposition is

$$RSH + Au(0)_n \xrightarrow{[O]} RS^-Au(I)/Au(0)_{n-1} \qquad (1)$$
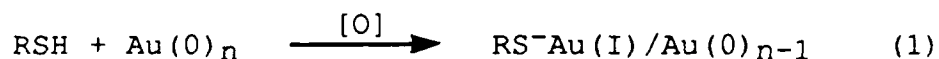
consistent with the observation that the gold remaining on
the sulfur-terminated monolayer was oxidized relative to
Au(0).

We have not been able to establish whether the gold
remaining on these monolayers after adhesive failure was
organized in microscopic islands. The amount of residual
gold on the silicon substrates was too small to permit the
use of scanning Auger to map its distribution. In the XPS
spectrum, however, the observation of a single, oxidized gold
environment suggests that the gold on the surface after
adhesive failure was present as a monolayer. If the gold had
been present in relatively thick (> 100 Å) islands, the
binding energy of the gold would have been that of bulk Au(0)
and any oxidized layer would, because of its low intensity,
have been unobservable.

Gold adhered to both the thiol- and thioacetate-
terminated monolayers. The XPS spectra suggest that, despite
the differences in the constitution of the initial
monolayers, the chemical composition of the monolayer-gold
interface after deposition of the gold film was the same for
these two systems. The sulfur and gold in these two systems
exhibited experimentally indistinguishable binding energies
and the acetyl ($-COCH_3$) group had disappeared from the
thioacetate. While the chemical processes that result in
loss of acetyl during reaction of gold with the thioacetate
are unknown, it appears that the mechanism of adhesion for
gold on the thiol- and thioacetate-terminated monolayers
involved the same chemical bond.

Acknowledgments

Experimental Section

General. Chemicals: 11-bromoundecene (Pfaltz and
Bauer), thiolacetic acid (Aldrich), dihydrogenhexa-
chloroplatinate(II) (Alfa), and trichlorosilane (Petrarch)
were used as received. Methylene chloride was distilled from
CaH_2. Chloroform (Mallinckrodt), absolute ethanol (USI),
diethyl ether (Mallinckrodt), and hexanes (Fisher) were used
as received.

10-Undecenyl Thioacetate. Sodium (2.2 g, 97 mg-atom)
was dissolved in absolute ethanol (200 mL) in a 500-mL round-
bottomed flask equipped with a side-arm. The flask was
sealed with a septum and the solution was purged of dioxygen
by bubbling argon gas through it. Thiolacetic acid (7.8 mL,
109 mmol) was added with a gas-tight syringe. The solution
was stirred for 30 min, after which 11-bromoundecene (13.9 g,
60 mmol) was added. The solution was heated at reflux
(135 min) and stirred for a further 15 h. The solvent was
evaporated and the remaining oil was dissolved in 200 mL of
hexane. This solution was extracted with water (2 x 200 mL).
The aqueous extracts were combined and extracted with hexane
(100 mL) which was added to the original organic solution.
The solvent was evaporated and the resulting oil was eluted
with 93:7 (v/v) hexanes/ether through a silica column
(230-400 mesh, diameter-4 cm, length-50 cm). The fractions
that contained the product were combined and the solvent was
evaporated. The remaining oil was distilled in a Kugelrohr
apparatus. A fraction was collected that boiled between

53 °C(0.003 torr) and 74 °C(0.008 torr): The product

(11.6 g, 51 mmol, 85%) was isolated as a yellow oil.

^{1}H NMR (CDCl3): δ 5.8 (m,1), 4.9 (m,2), 2.8 (t,2), 2.3 (s,3),

2.0 (m,2), 1.5 (m,2), 1.4-1.2 (m,14). Anal. Calcd. for

$C_{13}H_{24}OS$: C, 68.35; H, 10.61; S, 14.03. Found: C, 68.30;

H, 10.75; S, 14.12.

11-Trichlorosilylundecyl Thioacetate (1). This

compound was prepared by hydrosilylation[34] of 10-undecenyl

thioacetate. Trichlorosilane (3.6 mL, 36 mmol),

10-undecenyl thioacetate (5.0 g, 22 mmol), and dihydrogen-

hexachloroplatinate(II) (2.5 mL of a 0.01 M solution in THF,

0.025 mmol) were placed under argon in a dry heavy-walled

glass tube (diameter-2.5 cm, length-21 cm) equipped with a

sidearm, a 0-10 mm Teflon® stopcock, and a stirring bar. The

solution was degassed (freeze-pump-thaw, 3 cycles) and the

tube was sealed under vacuum at -195 °C. The tube was then

warmed to room temperature and heated in an oil bath (98 °C,

41 h). After the tube had been cooled to -195 °C, a liquid

nitrogen-cooled condenser was attached. The product was then

warmed to room temperature and the excess trichlorosilane

removed by a trap-to-trap distillation. The remaining liquid

was transferred to a dry Kugelrohr distillation apparatus and

a fraction was collected that boiled between 70 °C(0.004

torr) and 112 °C(0.005 torr). This crude material (7.09 g)

was then distilled in a dry short-path still and the fraction

that boiled between 112 °C(.026 torr) and 122 °C(.024 torr)

was collected. The product (4.48 g, 12 mmol, 56%) was

isolated as a clear oil. ^{1}H NMR (CDCl$_3$): δ 2.8 (t,2),

2.3 (s,3), 1.7-1.2 (m,20). ^{13}C NMR (CDCl$_3$): δ 195.1, 31.69,

30.46, 29.43, 29.36, 29.31, 29.21, 29.06, 28.99, 28.89,

28.72, 24.28, 22.20. Anal. Calcd. for C$_{13}$H$_{25}$Cl$_3$OSSi:

C, 42.91; H, 6.94; Cl, 29.23; S, 8.81. Found: C, 42.88;

H, 6.89; Cl, 29.30; S, 8.90.

Preparation of Monolayers. Silicon (100) substrates

were standard boron-doped semiconductor grade silicon in

3 in. diameter wafers from Monsanto. The wafers were cut

into 4 x 1.5-cm strips. These strips were cleaned by heating

in a solution of conc. H$_2$SO$_4$ and 30% H$_2$O$_2$ (70:30 v/v) at

90 °C for 30 min.[18] (Caution: 'piranha solution' reacts

violently with many organic materials and should be handled

with great care.) The substrates were rinsed with doubly-

distilled water and stored under water until use.

Solutions of **1** in methylene chloride (~ 1 mM) were

prepared in a dry, nitrogen atmosphere. The substrates were

placed in solution for 24 h and then rinsed in CH$_2$Cl$_2$. After

this wash the substrates were removed from the dry atmosphere

and rinsed in CHCl$_3$ and ethanol to remove any organic

contaminants. The sample was then rinsed with ethanol

dispensed from a pipette. The monolayer was dried under a

stream of argon and contact angle and ellipsometry

measurements were made immediately.

Hydrolysis. The substrates with the thioacetate-

terminated monolayers were hydrolyzed in conc. HCl at 70 °C

for 1.5 h. The wafers were removed from the acidic solution,

rinsed with distilled water (2 x 20 mL) and ethanol
(2 x 20 mL) and dried under a stream of argon.

   Characterization.   Contact angles were measured on
sessile drops using a Ramé-Hart Model 100 contact angle
goniometer equipped with a controlled environment chamber.
All measurements were made at > 80% relative humidity on 3-μL
drops. The reported values are an average of eight
measurements and have a precision of $\pm$ 3°. Ellipsometric
data were determined with a Rudolph Research Model 43603-200E
thin film ellipsometer equipped with a He-Ne laser
(λ = 6328 Å). The angle of incidence was 70.0° and the
compensator was set at -45°. Analyzer (A) and polarizer (P)
angles in zones 1 and 3 were determined for both the silicon
substrate and for the substrate coated with a monolayer film.
Values for A and P were averages from four different
locations on the sample separated by at least 1 cm. The
individual angles had a maximum scatter of 0.15°. The four
locations were, by visual inspection, approximately the same
for the bare substrate and for the monolayer. The refractive
index for each substrate was determined from A and P for that
substrate. The thicknesses of the monolayers were estimated
using the algorithm of McCrackin[35] assuming a refractive
index of 1.45 for the monolayer. Although the thioacetate
group probably has a refractive index different from the
hydrocarbon in the monolayer, the error introduced into the
estimation of the thickness by assuming a homogeneous
monolayer is less than 1 Å.

XPS spectra were acquired with a Surface Science Laboratories Model SSX-100 spectrometer with a monochromatized Al K_α X-ray source (10^{-8}-10^{-9} torr). Spectra were referenced to Au $4f_{7/2}$ at 84.0 eV. For each sample a survey spectrum (resolution 1.1 eV, spot size 1000 μm, 1 scan) and high resolution spectra (resolution 0.16 eV, spot size 300 μm, 10-30 scans) of the C 1s, O 1s, Si 2p, S 2s, and Au 4f regions were taken. Atomic compositions were determined using standard multiplex fitting routines with the following sensitivity factors: C 1s, 1.00; Si 2p, 0.90; O 1s, 2.49; S 2s, 1.48; Au 4f, 19.08.[36] Binding energies were referenced to an average of the C 1s, Si 2p and O 1s signals. Changes in the binding energies due to shifts in the reference were less than 0.2 $\pm$ 0.1 eV.

Electron micrographs were obtained with a JEOL JSM-35 scanning electron microscope.

Gold Evaporation. Gold layers were prepared by downward thermal evaporation. Evaporations were performed at 4 x 10^{-7} torr at rates of 2.5 and 10 Å/sec. The thickness of the gold was monitored using an oscillating quartz crystal.

Adhesion Tests. Peel strengths were measured using an Instron model 1101 tester. Because the silicon substrates were fragile, they were glued to aluminum pieces before attachment to the instrument. Strips of consumer grade Scotch™-brand Magic tape (cat. no. 105) were applied to the surface and, using a cotton swab, pressed into intimate

contact with the gold. Adhesive strengths were measured for a 180° peel test at rates of 1 and 100 mm/min.

References and Notes

1. G. Upite, S. Varenca, Tezisy Dokl. Vses. Simp. Akt. Pverkhn. Tel **2**, 55 (1977), Chem. Abstr. **92**, 14451j (1980).

2. K. H. Muecke, Metalloberfläche **31**, 506 (1977), Chem. Abstr. **88**, 31077b (1978).

3. Fujitsu Ltd., Japanese Patent 48/98732 (1983), Chem. Abstr. **101**, 63762z (1984).

4. G. J. Zydzik, L. G. Van Uitert, S. Singh, T. R. Kyle, Appl. Phys. Lett. **31**, 697 (1977).

5. I. V. Mitchell, J. S. Williams, P. Smith, R. G. Elliman, Appl. Phys. Lett. **44**, 193 (1984).

6. B. T. Werner, T. Vreeland Jr., M. H. Mendenhall, Y. Qui, T. A. Tombrello, Thin Solid Films **104**, 163 (1983).

7. J. E. Griffith, Y. Qui, T. A. Tombrello, Nucl. Instrm. Methods Phys. Res. **198**, 607 (1982), Chem Abstr. **97**, 119011x (1982).

8. M. K. Chaudhury, E. P. Plueddemann, J. Adhesion Sci. Tech. **1**, 243 (1987).

9. R. G. Nuzzo, D. L. Allara, J. Am. Chem. Soc. **105**, 4481 (1983).

10. C. D. Bain, E. B. Troughton, Y.-T. Tao, J. Evall, G. M. Whitesides, J. Am. Chem. Soc. **111**, 321 (1989).

11. M. D. Porter, T. B. Bright, D. L. Allara, C. E. D. Chidsey, J. Am. Chem. Soc. **109**, 3559 (1987).

12. E. B. Troughton, C. D. Bain, G. M. Whitesides, R. G. Nuzzo, D. L. Allara, M. D. Porter, Langmuir **4**, 365 (1988).

13. R. G. Nuzzo, B. R. Zegarski, L. H. Dubois, J. Am. Chem. Soc. **109**, 733 (1987).

14. Stable bis(alkylthiolate) gold(I) salts ($Au(SR)_2^-$) have been prepared by reaction of Au(I) dihalides with alkylthiolates. G. A. Bowmaker, B. C. Dobson, J. Chem. Soc., Dalton Trans., 267 (1981).

15. D. L. Allara, A. F. Heburd, F. J. Padden, R. G. Nuzzo, D. R. Falcon, J. Vac. Sci. Technol. A, 376 (1983).

16. D. L. Allara, R. G. Nuzzo, U. S. Patent 4690715 (1987).

17. K. R. Stewart, G. M. Whitesides, H. P. Godfried, I. F. Silvera, Rev. Sci. Instrum. **57**, 1381 (1986).

18. F. Pintchovski, J. B. Price, P. J. Tobin, J. Peavey, K. Kobold, J. Electrochem. Soc. **126**, 1428 (1979).

19. Solutions of **1** were used within 48 h of preparation. While a rigorously dry atmosphere was not required, too high a water content in the atmosphere resulted in polymerization and precipitation of the starting silane.

20. S. R. Wasserman, Y.-T. Tao, G. M. Whitesides, Langmuir, in press.

21. The thioacetate was subjected to acidic rather than basic hydrolysis since monolayers from alkyltrichlorosilanes are not stable in base.

22. This range is not significant. Ellipsometric measurements for organic monolayers on silicon have a precision of $\pm$ 2 Å.

23. Monolayers prepared from methyl-terminated alkyltrichlorosilanes are apparently oriented nearly perpendicular (tilt angle $\approx$ 14 $\pm$ 18°) to the substrate surface in a _trans_-extended chain. R. Maoz, J. Sagiv, J. Colloid Interface Sci. **100**, 465 (1984). N. Tillman, A. Ulman, J. S. Schildkraut, T. L. Penner, J. Am. Chem. Soc. **110**, 6136 (1988).

24. S. R. Wasserman, G. M. Whitesides, I. M. Tidswell, B. Ocko, P. S. Pershan, J. D. Axe, J. Am. Chem. Soc., in press.

25. The bond lengths of typical C-S and C-C bonds are 1.85 and 1.54 Å respectively. Assuming a bond angle of 120°, we would predict a decrease of 2.93 Å upon hydrolysis of the thioacetate group in a completely formed monolayer. For the partial monolayers studied here, this predicted change must be corrected for the fractional coverage of the surface, in this case approximately 60%. For these monolayers the expected change in length would therefore be approximately 2 Å. R. C. Weast, Ed., CRC Handbook of Chemistry and Physics (CRC Press, Boca Raton, Florida, 1984), 65th ed., pp. F-166-F-167.

26. C. D. Bain, H. A. Biebuyck, G. M. Whitesides, Langmuir, in press.

27. We do not know whether this binding energy indicates the presence of a thiol or of a disulfide. The difference in the binding energies of the S 2p electrons in a thiol (163.3 eV) and a disulfide (163.0 eV) is small. Values for the S 2s electrons are expected to differ by similar amounts. The difference in these binding energies is similar to the errors in our reference peaks. See references 13 and 26.

28. Adhesive failure for the thiol-terminated monolayers occurred, on average, in ~ 15% of the total area covered by the tape. On individual samples failure was found over 2 - 50% of the surface. For the thioacetate-terminated monolayers, failure occurred only on 25% of the samples, removed gold from less than 1% of the area covered by the tape. We believe that this difference in failure rates probably reflects contamination of the thiol interface during the hydrolysis of the thioacetate group.

29. Since the monolayers prepared from HTS were longer than those created from **1**, the Au/C ratio exaggerates the difference in the amount of gold left on these surfaces. Comparisons to the Si 2p signal, which underestimates this difference, indicate that at least six times as much gold was left on the thiol-terminated interface as on the methyl-terminated one.

30. The binding energy of the gold is referenced to an average of the C 1s, O 1s, and Si 2p signals.

31. The binding energy of the sulfur in the thiol-terminated monolayer (228.4 eV) was between that of the sulfur in the thioacetate group (228.7 eV) and that of the sulfur in the thiol bound to the gold (228.0 eV). Uncertainties in the reference peaks were, however, almost as large as this shift.

32. The difference in the 2p binding energy for a sulfur in a thiol group and that in a thiolate form (RS⁻) is ~ 2.8 eV. Values for the S 2s electrons are expected to differ by similar amounts. See reference 29.

33. G. K. Wertheim, S. B. DiCenzo, S. E. Youngquist, Phys. Rev. Lett. **51**, 2310 (1983).

34. E. Lukevics, Z. V. Belyakova, M. G. Pomerantseva, M. G. Voronkov, in <u>Journal of Organometallic Chemistry Library 5: Organometallic Chemistry Reviews</u>, D. Seyferth, A. G. Davies, E. O. Fischer, J. F. Normant, O. A. Reutov, Eds. (Elsevier, Amsterdam, 1977), pp. 1-179 and the references therein.

35. F. L. McCracken, E. Passaglia, R. R. Stromberg, H. L. Steinberg, J. Res. Natl. Bur. Stand., Sect. A. **67**, 363 (1963).

36. These sensitivities are those provided by Surface Science Laboratories in their ESCA 8.0B software. These sensitivities reflect both the inherent photoionization cross-section of each element and the dependence of the mean free path of an electron on its energy. J. H. Scofield, J. Electron Spectrosc. **8**, 129 (1976).

Captions

Scheme I. Synthesis of 11-trichlorosilylundecyl

thioacetate, **1**.

Figure 1. Schematic representation of the preparation of the

gold-silicon composite. (A) Formation of a

thioacetate-terminated monolayer on Si/SiO_2 by

reaction of $Cl_3Si(CH_2)_{11}SCOCH_3$ (**1**) in methylene

chloride solution with Si-OH groups and adsorbed

water on the surface of the substrate. (B)

Formation of a thiol-terminated monolayer by

acidic hydrolysis of the monolayer prepared in

step A. (C) Thermal evaporation of gold

(650-1000 Å) onto the thiol-terminated monolayer

prepared in step B. The molecular order in these

monolayer systems has not been defined, but the

monolayers were thinner (and thus probably more

disordered) than fully _trans_-extended chains

oriented perpendicular to the surface.

Figure 2. XPS spectra of monolayers prepared from
$Cl_3Si(CH_2)_{11}SCOCH_3$ (**1**) and $Cl_3Si(CH_2)_{15}CH_3$ (HTS)
on Si/SiO_2 substrates: survey spectra (left) and
high resolution spectra of the carbon 1s (left
center), sulfur 2s (right center), and gold 4f
(right) regions. Spectra are shown for these
monolayers prior to evaporation of gold onto the
sample (A,C,E) and for the monolayers that
remained after the gold had been removed from the
surface (B,D,F) (see text). Spectra are
referenced to an average of the binding energies
of the C 1s, Si 2p, and O 1s peaks. The C 1s and
S 2s spectra are each normalized to the same
maximum peak height. The Au 4f spectra are not
normalized; their intensities represent the
relative amounts of gold remaining on these
surfaces. The S 2s spectra have been smoothed
using a nine-point algorithm with a symmetrical
triangle convolution function. (A. Savitzky, A.
M. J. E. Golay, Anal. Chem. **36**, 1627 (1964).)
(A) Thioacetate-terminated monolayer prepared from
1. (B) A after removal of gold from the surface.
The survey and Au 4f spectra include bulk gold
(Au(0)) in the area surrounding the region of
adhesive failure. (C) Thiol-terminated monolayer
prepared by acidic hydrolysis (conc. HCl, 70 °C,

1.5 h) of A.   (D) C after removal of gold from the surface.   (E) Methyl-terminated monolayer prepared from HTS.   (F) E after removal of gold from the surface.

Figure 3. Electron micrographs of the border of the gold remaining after adhesive failure. The light regions are gold; the dark areas correspond to the Si/SiO_2 substrate. The shaded region to the left of each micrograph indicates that part of the field of view which had been covered by the tape. The size markers in the micrographs correspond to 100 μm. (A) Methyl-terminated monolayer prepared from $Cl_3Si(CH_2)_{15}CH_3$ (HTS). The arrow indicates the approximate position and direction of the edge of the tape before its removal. The edge of the gold corresponds to the edge of the tape. (B) Thiol-terminated monolayer prepared by acidic hydrolysis (conc. HCl, 70 °C, 1.5 h) of a monolayer prepared from $Cl_3Si(CH_2)_{11}SCOCH_3$ (**1**). The entire field of view was covered by the tape. The edge of the gold represents the border of the region where failure in adhesion had occurred, but it does not correspond to the edge of the tape.

TECHNICAL REPORT DISTRIBUTION LIST, GENERAL

	No. Copies		No. Copies
Office of Naval Research Chemistry Division, Code 1113 800 North Quincy Street Arlington, VA 22217-5000	3	Dr. Ronald L. Atkins Chemistry Division (Code 385) Naval Weapons Center China Lake, CA 93555-6001	1
Commanding Officer Naval Weapons Support Center Attn: Dr. Bernard E. Douda Crane, IN 47522-5050	1	Chief of Naval Research Special Assistant for Marine Corps Matters Code 00MC 800 North Quincy Street Arlington, VA 22217-5000	1
Dr. Richard W. Drisko Naval Civil Engineering Laboratory Code L52 Port Hueneme, California 93043	1	Dr. Bernadette Eichinger Naval Ship Systems Engineering Station Code 053	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	2 high quality	Philadelphia Naval Base Philadelphia, PA 19112	
David Taylor Research Center Dr. Eugene C. Fischer Annapolis, MD 21402-5067	1	Dr. Sachio Yamamoto Naval Ocean Systems Center Code 52 San Diego, CA 92152-5000	1
Dr. James S. Murday Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375-5000	1	David Taylor Research Center Dr. Harold H. Singerman Annapolis, MD 21402-5067 ATTN: Code 283	1

POLYMER PROGRAM DISTRIBUTION LIST

Dr. J. M. Augl
Naval Surface Weapons Center
White Oak, MD 20910

Dr. A. S. Abhiraman
School of Chemical Engineering
Georgia Institute of Technology
Atlanta, GA 30332

4132033

Dr. Harry R. Allcock
Department of Chemistry
Pennsylvania State University
University Park, PA 16802

4132007

Dr. Chris W. Allen
Department of Chemistry
University of Vermont
Burlington, VT 05405

413c012

Dr. Ronald D. Archer
Department of Chemistry
University of Massachusetts
Amherst, MA 01003

413c028

Dr. Ali S. Argon
Mechanical Engineering Department
Massachusetts Institute of Technology
Cambridge, MA 02139

a400005df

Dr. William J. Bailey
Department of Chemistry
University of Maryland
College Park, MD 20742

413a006

Dr. Kurt Baum
Fluorochem, Inc.
680 S. Ayon Avenue
Azusa, CA 91702

4000021sbi

Dr. Frank D. Blum
Department of Chemistry
University of Missouri - Rolla
Rolla, MO 65401

413m005

Dr. Len J. Buckley
Naval Air Development Center
Code 6063
Warminster, PA 18974

Dr. F. James Boerio
Materials Science & Engineering Dept.
University of Cincinnati
Cincinnati, Ohio 45221

413m012

Dr. Ivan Caplan
DTNSRDC Annapolis
Code 0125
Annapolis, MD 21401

Dr. Robert E. Cohen
Department of Chemical Engineering
Massachusetts Institute of Technology
Cambridge, MA 02139

4132001

Dr. E. Fischer
DTNSRDC Code 2853
Annapolis, MD 21402

Dr. Curtis W. Frank
Department of Chemical Engineering
Stanford University
Stanford, CA 94305

413h005

Dr. Gregory S. Girolami
School of Chemical Sciences
University of Illinois
Urbana-Champagne, IL 61801

4132014

Dr. Robert H. Grubbs
Department of Chemistry
California Institute of Technology
Pasadena, CA 91124

4132019

Dr. James F. Haw
Department of Chemistry
Texas A&M University
College Station, TX 77843

413c039

Dr. Stuart L. Cooper
Department of Chemical Engineering
University of Wisconsin
Madison, WI 53706

4132006

Dr. Warren T. Ford
Department of Chemistry
Oklahoma State University
Stillwater, OK 74078

413h006

Dr. John K. Gillham
Department of Chemical Engineering
Princeton University
Princeton, New Jersey 08544

413c005

Dr. Bernard Gordon
Department of Polymer Science
Pennsylvania State University
University Park, PA 16802

413c025

Dr. Henry K. Hall
Department of Chemistry
University of Arizona
Tucson, AZ 85721

413j009

Dr. Alan J. Heeger
Department of Physics
University of California, Santa Barbara
Santa Barbara, CA 93106

4132012

Dr. Pat J. Hendra
Department of Chemistry
University of Southampton
Highfield Southampton 509 5NH
United Kingdom
4134001

Dr. Charles E. Hoyle
Department of Polymer Science
University of Southern Mississippi
Hattiesburg, MS 39406-0076

413c026

Dr. Bruce S. Hudson
Department of Chemistry
University of Oregon
Eugene, Oregon 97403

413c018

Dr. Leonard V. Interrante
Department of Chemistry
Rensselaer Polytechnic Institute
Troy, NY 12181

413c014

Dr. Hatsuo Ishida
Department of Macromolecular Science
Case Western Reserve University
Cleveland, OH 44106

413m008

Dr. Jeffrey T. Koberstein
Institute of Materials Science
University of Connecticut
Storrs, CT 06268

4132013

Dr. Paul M. Lahti
Department of Chemistry
University of Massachusetts
Amherst, MA 01003

413c037

Dr. Richard M. Laine
Washington Technology Center
University of Washington
Seattle, WA 98195

s400033srh

Dr. Robert W. Lenz
Polymer Science and Engineering Dept.
University of Massachusetts
Amherst, MA 01002

441c013

Dr. Geoffrey Lindsay
Chemistry Division - Code 087
Naval Weapons Center
China Lake, CA 93555

4132036

Dr. Alan D. MacDiarmid
Department of Chemistry
University of Pennsylvania
Philadelphia, PA 19104

a400004df

Dr. Chris W. Macosko
Materials Science & Engineering Dept.
University of Minnesota
Minneapolis, MN 55455

4132029

Dr. Joseph H. Magill
Materials Science & Engineering Dept.
University of Pittsburgh
Pittsburgh, PA 15161

413c013

Dr. Tobin J. Marks
Department of Chemistry
Northwestern University
Evanston, IL 60201

413c030

Dr. Krzysztof Matyjaszewski
Department of Chemistry
Carnegie Mellon University
Pittsburgh, PA 15213

413j002

Dr. William B. Moniz
Code 6120
Naval Research Laboratory
Washington, DC 20375-5000

4132012

Dr. Virgil Percec
Department of Macromolecular Science
Case Western Reserve University
Cleveland, OH 44106-2699

413c024

Dr. Roger S. Porter
Dept. of Polymer Science & Engineering
University of Massachusetts
Amherst, MA 01002

413m006

Dr. Leo Mandelkern
Department of Chemistry
Florida State University
Tallahasee, FL 32306-3015

4132018

Dr. Lon J. Mathias
Department of Polymer Science
University of Southern Mississippi
Hattiesburg, MS 30406-0076

413m003

Dr. James E. McGrath
Department of Chemistry
Virginia Polytechnic Institute
Blacksburg, VA 24061

4132007

Dr. Kay L. Paciorek
Ultrasystems Defense and Space, Inc.
16775 Von Karman Avenue
Irvine, CA 92714

s400029srh

Dr. Martin Pomerantz
Department of Chemistry
University of Texas at Arlington
Box 19065
Arlington, TX 76019-0065
a400008df

Dr. T. J. Reinhart, Jr.
Nonmetallic Materials Division
Air Force Materials Laboratory (AFSC)
Wright-Patterson AFB, OH 45433

Dr. Arnost Reiser
Insitute of Imaging Sciences
Polytechnic University
333 Jay Street
Brooklyn, NY 11021

4132022

Dr. Charles M. Roland
Code 6120
Naval Research Laboratory
Washington, DC 20375-5000

413m009

Dr. Ronald Salovey
Department of Chemical Engineering
University of Southern California
Los Angeles, CA 90089

413m010

Dr. Jerry I. Scheinbeim
Dept. of Mechanics & Materials Science
Rutgers University
Piscataway, NJ 08854

4132009

Dr. L. E. Sloter
Code Air 931-A
Naval Air Systems Command
Washington, D. C. 20361-9310

Dr. Dietmar Seyferth
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, MA 02139

413c004

Dr. Ferdinand Rodriguez
Department of Chemical Engineering
Cornell University
Ithaca, NY 14853

413c011

Dr. Michael F. Rubner
Materials Science & Engineering Dept.
Massachusetts Institute of Technology
Cambridge, MA 02139

413m007

Dr. Jacob Schaefer
Department of Chemistry
Washington University
St. Louis, MO 63130

413m001

Dr. Lawrence R. Sita
Department of Chemistry
Carnegie Mellon University
Pittsburgh, PA 15213

4132030

Dr. Richard R. Schrock
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, MA 02139

4132038

Dr. David S. Soane
Department of Chemical Engineering
University of California, Berkeley
Berkeley, CA 94720-9989

413h004

Dr. Les H. Sperling
Materials Research Center #32
Lehigh University
Bethlehem, PA 18015

413c002

Dr. C. S. Sung
Institute of Materials Science
University of Connecticut
Storrs, CT 06268

413m011

Dr. C. H. Wang
Department of Chemistry
University of Utah
Salt Lake City, Utah 84112

413c020

Dr. Robert A. Weiss
Department of Chemical Engineering
University of Connecticut
Storrs, CT 06268

a400006df

Dr. Garth L. Wilkes
Department of Chemical Engineering
Virginia Polytechnic Institute
Blacksburg, VA 24061

4132020

Dr. Richard S. Stein
Polymer Research Institute
University of Massachusetts
Amherst, MA 01002

4132008

Dr. Sukant K. Tripathy
Department of Chemistry
University of Lowell
Lowell, MA 01854

4132016

Dr. Kenneth B. Wagener
Department of Chemistry
University of Florida
Gainesville, FL 32611

a400007df

Dr. George M. Whitesides
Department of Chemistry
Harvard University
Cambridge, MA 02138

4132010